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The dynamical matrix for graphene

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In frame of De Launay model, the expression for elements of dynamical matrix of graphene have been deduced with accounting interatomic forces on the first six neighbor atoms. The calculation of phonon dispersion of graphene in ГК and ГМ directions is done via known values of radial and tangential force constants on the first five neighbor atoms. Calculated phonon dispersion is in satisfactory agreement with experimental phonon spectra of graphite measured by another authors. In long wave approximation, the equations for estimation of elastic constants of graphene have been obtained from the expressions of elements of dynamical matrix.
Keywords: graphene, dynamical matrix, phonon dispersion, elastic constants.

Динамічна матриця для графену. *Г. Мягмарсурен , Ц. Амартайван, Ц.Гантулга, Л.Енхтор, І.Притула*

В рамках моделі Де Лане отримані вирази для елементів динамічної матриці графена з урахуванням міжатомної взаємодії перших шести сусідніх атомах. З використанням відомих значень радіальних та тангенціальних силових постійних для перших п'яти сусідніх атомів розрахована дисперсія фононів у напрямках ГК та ГМ, яка задовільно збігається з експериментальним фононним спектром графіту, виміряним іншими авторами. У довгохвильовому наближенні виразів для елементів динамічної матриці отримані формули для оцінки пружних постійних графена.

1. Introduction

Several models applied to description of the dynamical matrix of graphene and carbon nanotubes [1-3]. The expressions for elements of dynamical matrix in frame of De Launay model were described for carbon nanotubes and used for estimations of elastic constant, Yong modulus, and Poissons ratio via data of Raman frequencies [1]. In framework of the Born-von Karman model, Falcovsky suggested elements of dynamical matrix via force constants of graphite on first three neighbor atoms [2]. Using its Falcovsky calculated phonon dispersion of graphene in high-symmetry directions but did not compare with experimental phonon spectra of graphite. Gray et. al [3] on the background of the Born model obtained expressions for elements of dynamical matrix of graphene, by fitting of experimental phonon dispersion of graphite [4] estimated force constants on first the shell and using its calculated phonon dispersion in high symmetry directions. But calculated phonon dispersion is different from the experimental phonon dispersion of graphite [4].

In this work, we developed the De Launay model for description of dynamical matrix of graphene. The calculations of phonon dispersion and elastic constants of graphene are done in comparison with experimental results [4,5].

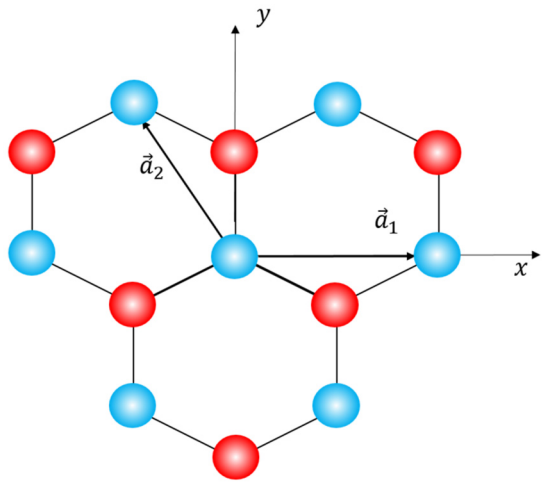

Fig.1 Crystal structure of graphene layer. There are two atoms in unit cell.

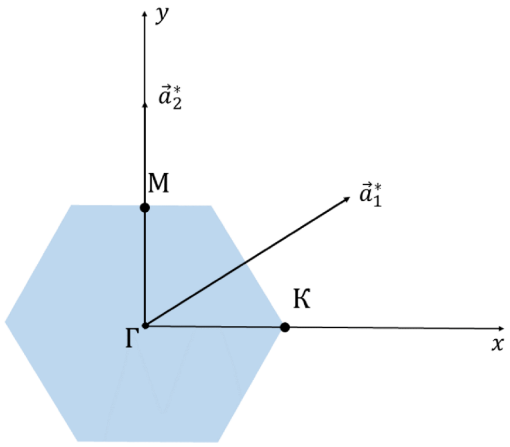

Fig. 2 First Brillouin zone of graphene.

2. Dynamical matrix of graphene

The two-dimensional crystal structure of graphene shown in Fig.1. It has two sublattices: red balls belong to the first sublattice, and blue balls belong to the second sublattice. The translation vectors $\vec{a}_1$ and $\vec{a}_2$ have absolute value of $a = a_0\sqrt{3}$ where $a_0 = 1.42+$ is distance between nearest atoms. In Fig. 2 shown first Brillouin zone of graphene. The high-symmetry points Γ, K and M are shown. Distance between points Γ-K is $4\pi/3a$, and distance Γ-M is $2\pi/a\sqrt{3}$.

The dynamical matrix of graphene layer for in-plane vibrations has the form:

$$\begin{bmatrix} D_{xx}^{AA} & D_{xy}^{AA} & D_{xx}^{AB} & D_{xy}^{AB} \\ D_{xy}^{AA} & D_{yy}^{AA} & D_{xy}^{AB} & D_{yy}^{AB} \\ D_{xx}^{AB*} & D_{xy}^{AB*} & D_{xx}^{AA} & D_{xy}^{AA} \\ D_{xy}^{AB*} & D_{yy}^{AB*} & D_{xy}^{AA} & D_{yy}^{AA} \end{bmatrix}.$$

The dynamical matrix for out-plane vibrations has the form:

$$\begin{bmatrix} D_{zz}^{AA} & D_{zz}^{AB} \\ D_{zz}^{AB*} & D_{zz}^{AA} \end{bmatrix}.$$

In frame of De Launay model [6] we derived expressions for the elements of dynamical matrix of graphene with accounting interatomic interaction in the first six neighbor atoms. There are

$$D_{xx}^{AA} = \frac{3}{2}\alpha_1 + \frac{3}{2}\beta_1 + 2\alpha_2\left\{1-\cos\left(aq_x\right)\right\} +$$

$$+\left(\alpha_2+3\beta_2\right)\left\{1-\cos\left(\frac{1}{2}aq_x\right)\cos\left(\frac{\sqrt{3}}{2}aq_y\right)\right\} + \frac{3}{2}\alpha_3 + \frac{3}{2}\beta_3 -$$

$$+3\alpha_4 + 3\beta_4 + 3\alpha_5 + 3\beta_5 - \left(3\alpha_5+\beta_5\right)\cos\left(\frac{3}{2}aq_x\right)\cos\left(\frac{\sqrt{3}}{2}aq_y\right) - 2\beta_5\cos\left(\sqrt{3}aq_y\right)$$

$$+2\alpha_6\left\{1-\cos\left(2aq_x\right)\right\} + \left(\alpha_6+3\beta_6\right)\left\{1-\cos\left(aq_x\right)\cos\left(\sqrt{3}aq_y\right)\right\};$$

$$D_{xx}^{AB} = -\beta_1 e^{-i\frac{1}{\sqrt{3}}aq_y} - \left(\frac{3}{2}\alpha_1 + \frac{1}{2}\beta_1\right)\cos\left(\frac{1}{2}aq_x\right)e^{i\frac{a}{2\sqrt{3}}aq_y} -$$

$$-\beta_3 e^{i\frac{2}{\sqrt{3}}aq_y} - \left(\frac{3}{2}\alpha_3 + \frac{1}{2}\beta_3\right)\left\{\cos\left(aq_x\right)e^{-i\frac{1}{\sqrt{3}}aq_y}\right\} +$$

$$-\left(\frac{3}{14}\alpha_4 + \frac{25}{14}\beta_4\right)\cos\left(\frac{1}{2}aq_x\right)e^{-i\frac{5}{2\sqrt{3}}aq_y} - \left(\frac{27}{14}\alpha_4 + \frac{1}{14}\beta_4\right)\cos\left(\frac{3}{2}aq_x\right)e^{i\frac{1}{2\sqrt{3}}aq_y} -$$

$$-\left(\frac{6}{7}\alpha_4 + \frac{8}{7}\beta_4\right)\cos\left(aq_x\right)e^{i\frac{2}{\sqrt{3}}aq_y} \ ;$$

$$D_{xy}^{AA} = \sqrt{3}\left(\alpha_2 - \beta_2\right)\sin\left(\frac{1}{2}aq_x\right)\sin\left(\frac{\sqrt{3}}{2}aq_y\right) + \sqrt{3}\left(\alpha_5 - \beta_5\right)\sin\left(\frac{3}{2}aq_x\right)\sin\left(\frac{\sqrt{3}}{2}aq_y\right) -$$

$$+\sqrt{3}\left(\alpha_6 - \beta_6\right)\sin\left(aq_x\right)\sin\left(\sqrt{3}aq_y\right);$$

$$D_{xy}^{AB} = -i\frac{\sqrt{3}}{2}\left(\alpha_1 - \beta_1\right)\sin\left(\frac{1}{2}aq_x\right)e^{i\frac{a}{2\sqrt{3}}q_y} +$$

$$+i\frac{\sqrt{3}}{2}\left(\alpha_3 - \beta_3\right)\ \sin\left(aq_x\right)e^{-i\frac{1}{\sqrt{3}}aq_y} + i\frac{5\sqrt{3}}{14}\left(\alpha_4 - \beta_4\right)\sin\left(\frac{1}{2}aq_x\right)e^{-i\frac{5}{2\sqrt{3}}aq_y} -$$

$$-i\frac{4\sqrt{3}}{7}\left(\alpha_4 - \beta_4\right)\sin\left(aq_x\right)e^{i\frac{2}{\sqrt{3}}aq_y} - i\frac{3\sqrt{3}}{14}\left(\alpha_4 - \beta_4\right)\sin\left(\frac{3}{2}aq_x\right)e^{i\frac{1}{2\sqrt{3}}aq_y}\Bigg\};$$

$$D_{yy}^{AA} = +\frac{3}{2}\alpha_1 + \frac{3}{2}\beta_1 + 2\beta_2\left\{1 - \cos\left(aq_x\right)\right\} +$$

$$+\left(3\alpha_2 + \beta_2\right)\left\{1 - \cos\left(\frac{1}{2}aq_x\right)\cos\left(\frac{\sqrt{3}}{2}aq_y\right)\right\} + \frac{3}{2}\alpha_3 + \frac{3}{2}\beta_3 + 3\alpha_4 + 3\beta_4 +$$

$$+3\alpha_5 + 3\beta_5 - \left(\alpha_5 + 3\beta_5\right)\cos\left(\frac{3}{2}aq_x\right)\cos\left(\frac{\sqrt{3}}{2}aq_y\right) - 2\alpha_5\cos\left(\sqrt{3}aq_y\right) +$$

$$+2\beta_6\left\{1 - \cos\left(2aq_x\right)\right\} + \left(3\alpha_6 + \beta_6\right)\left\{1 - \cos\left(aq_x\right)\cos\left(\sqrt{3}aq_y\right)\right\};$$

$$D_{yy}^{AB} = -\alpha_1 e^{-i\frac{1}{\sqrt{3}}aq_y} - \left(\frac{1}{2}\alpha_1 + \frac{3}{2}\beta_1\right)\cos\left(\frac{1}{2}aq_x\right)e^{i\frac{1}{2\sqrt{3}}aq_y} +$$

$$-\left(\frac{1}{2}\alpha_3 + \frac{3}{2}\beta_3\right)\cos\left(aq_x\right)e^{-i\frac{1}{\sqrt{3}}aq_y} - \alpha_3 e^{i\frac{2}{\sqrt{3}}aq_y} -$$

$$-\left(\frac{25}{14}\alpha_4 + \frac{3}{14}\beta_4\right)\cos\left(\frac{1}{2}aq_x\right)e^{-i\frac{5}{2\sqrt{3}}aq_y} - \left(\frac{1}{14}\alpha_4 + \frac{27}{14}\beta_4\right)\cos\left(\frac{3}{2}aq_x\right)e^{i\frac{1}{2\sqrt{3}}aq_y} -$$

$$-\left(\frac{8}{7}\alpha_4 + \frac{6}{7}\beta_4\right)\cos\left(aq_x\right)e^{i\frac{2}{\sqrt{3}}aq_y};$$

$$D_{zz}^{AA} = 3\gamma_1 + 2\gamma_2\left\{1 - \cos\left(aq_x\right)\right\} + 4\gamma_2\left\{1 - \cos\left(\frac{1}{2}aq_x\right)\cos\left(\frac{\sqrt{3}}{2}aq_y\right)\right\} + 3\gamma_3 + 6\gamma_4 +$$

$$+2\gamma_5\left\{3 - 2\cos\left(\frac{3}{2}aq_x\right)\cos\left(\frac{\sqrt{3}}{2}aq_y\right) - \cos\left(\sqrt{3}aq_y\right)\right\} -$$

$$+2\beta_6\left\{3 - 2\cos\left(aq_x\right)\cos\left(\sqrt{3}aq_y\right) - \cos\left(2aq_x\right)\right\};$$

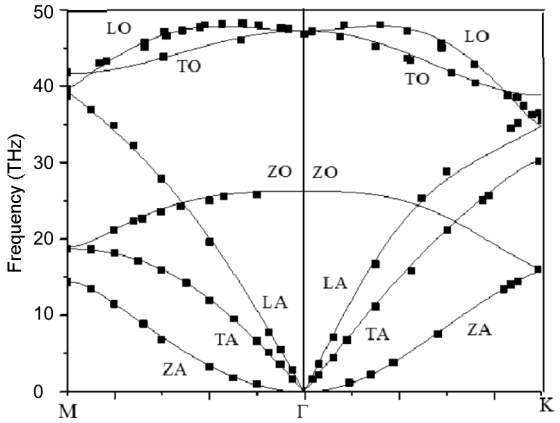

Fig. 3 Calculated phonon dispersion for graphene in directions of symmetry. For comparison, experimental data of phonon frequencies of graphite is shown [4]. The solid lines represent calculated dispersion curve, the black squares depict the experimental phonon frequencies of graphite.

$$D_{zz}^{AB} = -\gamma_1\left\{2\cos\left(\frac{1}{2}aq_x\right)e^{i\frac{1}{2\sqrt{3}}aq_y} + e^{-i\frac{1}{\sqrt{3}}aq_y}\right\} - \gamma_3\left\{2\cos\left(aq_x\right)e^{-i\frac{1}{\sqrt{3}}aq_y} + e^{i\frac{2}{\sqrt{3}}aq_y}\right\} -$$
$$-2\gamma_4\left\{\cos\left(\frac{1}{2}aq_x\right)e^{-i\frac{5}{2\sqrt{3}}aq_y} + \cos\left(aq_x\right)e^{i\frac{2}{\sqrt{3}}aq_y} + \cos\left(\frac{3}{2}aq_x\right)e^{i\frac{1}{2\sqrt{3}}aq_y}\right\};$$

$$D_{xy}^{AA} = D_{yx}^{AA}; D_{xy}^{AB} = D_{yx}^{AB}.$$

Where q_x and q_y are components of wave vector $\mathbf{q}$, α_i is radial force constant, β_i is tangential force constant (in plane), γ_i is tangential force constant (out plane), i =1,2,...,6.

3. Results of calculations and discussion

The dispersion of phonon frequencies $\nu(\mathbf{q})$ in symmetric directions can be calculated by solution of secular equation:

$$\left|D(\mathbf{q}) - 4\pi^2 m\nu^2 I\right| = 0,$$

where $D(\mathbf{q})$ is dynamical matrix, I is the unity matrix, m is the atomic mass. For verification of suggested expressions for elements of dynamical matrix, we calculated the phonon dispersion of graphene along the high symmetry directions via set of known force constants [4]. In Fig. 3 shown calculated phonon dispersion of graphene along ΓK and ΓM directions in comparison with experimental data for graphite [4]. The calculated phonon dispersion curves are in satisfactory coincidence with experimental values of phonon frequencies of graphite [4].

For estimation of elastic constants of graphene, from the expressions of dynamical matrix in longwave approximation (q→0) we derived following equations:

$$c_{11} = \frac{a^2\rho}{m}\left(\frac{3}{16}\alpha_1 + \frac{1}{16}\beta_1 + \frac{9}{8}\alpha_2 + \frac{3}{8}\beta_2 + \frac{3}{4}\alpha_3 + \frac{1}{4}\beta_3 + \frac{21}{8}\alpha_4 + \frac{7}{8}\beta_4 + \frac{27}{8}\alpha_5 + \frac{9}{8}\beta_5\right);$$

$$\frac{1}{2}\left(c_{11} - c_{12}\right) = \frac{a^2\rho}{m}\left(\frac{1}{16}\alpha_1 + \frac{3}{16}\beta_1 + \frac{3}{8}\alpha_2 + \frac{9}{8}\beta_2 + \frac{1}{4}\alpha_3 + \frac{3}{4}\beta_3 + \frac{7}{8}\alpha_4 + \frac{1}{8}\beta_4 + \frac{9}{8}\alpha_5 + \frac{27}{8}\beta_5\right);$$

$$c_{44} = \frac{a^2\rho}{m}\left(\frac{1}{4}\gamma_1 + \frac{3}{2}\gamma_2 + \gamma_3 + \frac{21}{2}\gamma_4 + \frac{9}{2}\gamma_5\right).$$

Where m=12.0107 u is atomic mass of carbon, ρ =2.266 g/cm^3 is density of graphite. We calculated by these equations elastic constants for graphene via radial and tangential force constants for first five neighbor atoms [4]. The results of calculations are given in Table 1 in comparison with the experimental data for graphite [5] and results of calculations for graphene [2]. Calculated in

Table 1. Elastic constants for graphite and graphene (10^9 N/m^2)

	C_{11}	C_{12}	C_{44}
Experiment for graphite [5]	106	18	0.035
Graphene [2]	86	18	0.57
Graphene [this work]	139.91	14.49	-0.05

this work values of C_{11} and C_{12} agree satisfactorily with experimental data for graphite. But the estimated value of C_{44} with opposite sign. The elastic constant C_{12} of graphene calculated by Falcovsky [2] coincides with experimental result of graphite, C_{11} agrees in order of magnitude with the experimental value for graphite.

4. Conclusion

New expressions for elements of dynamical matrix for graphene are suggested. Results of calculation of the phonon dispersion of graphene in high symmetry directions are in satisfactory coincidence with experimental data of graphite. Estimated values of elastic constant C_{11} and C_{12} for graphene are comparable with corresponding experimental values for graphite. Within the framework of the De Launay model, the possibility of calculating the lattice dynamics of the graphene has been shown.

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